High pressure phase diagrams of inorganic materials and metal alloy systems (Modern aspects of physical chemistry at high pressure : the 50th commemorative volume)

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HIGH PRESSURE PHASE DIAGRAMS OF INORGANIC MATERIALS AND METAL ALLOY SYSTEMS

By J. B. CLARK and P. W. RICHTER

Selected high pressure phase diagrams of inorganic materials are reviewed. Crystal chemical relationships for groups of related inorganic compounds are discussed.

The effect of pressure on binary metal alloy systems is discussed for certain selected examples. Behavioural trends are discussed for such systems.

1. Introduction

The determination of high pressure phase relations of a broad range of materials have been the focus of a large amount of research. The research has been carried out in a number of experimental devices and much of the data has been reviewed previously.[1,2]

The earliest studies of the effect of pressure on phase chages were done on the liquefaction of gases during the previous century.[3,4] Since then the ubiquity of the phenomena of phase transitions in solids have been thoroughly demonstrated. Studies of the effect of pressure on the melting point of solids are relatively few compared to studies of solid-solid phase transitions. However, extensive studies have been made of the character of solid-solid phase transitions and on the determination of the stability fields of various solid phases in the pressure-temperature plane. Various types of solid-solid phase transitions have been identified. Electronic phase transitions occur when application of pressure causes an electronic adjustment in a system. This involves the overlap of adjacent electron bands or delocalization of the electrons *e. g.*. the 4f electron in cerium.[5-7] Insulator to metal transitions may be either caused by electronic effects (Mott and Wilson band-overlap type transitions)[8-11] or by rearrangement in the lattice, *e. g.* the transition to the metallic state of the semiconducting group IV elements and related semiconductors.[12-14] Magnetic transitions such as the Rudermann-Kittel type exchange in rare-earth metals or the antiferromagnetic ordering that occurs, for example, in chromium and its alloys, involve the conduction eletcrons.[15] Jayaraman[16] discusses the influence of pressure on some of these phase transitions in more detail.

Structural phase transitions occur in a substance when the crystallographic lattice becomes unstable with respect to another arrangement of atoms, and a subsequent rearrangement of the atoms into a lattice with a lower Gibbs free energy results. The Gibbfree energy,

$$G = U - TS + PV$$

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determines phase stability, because the thermodynamically stable phase has the minimum Gibbs free energy under the given conditions. At higher temperatures and low pressure the entropy term dominates and lower density open structures are favoured. The PV term, however, becomes more important at high pressure and the stable phases are of high density and higher coordination.

The interpretation and prediction of pressure-temperature phase diagrams are largely empirical as it is not yet possible to predict these reliably from the basic principles of solid state theory. Pseudopotential, lattice dynamical[17-18] and *a priori* quantum[19] calculations have had varying degrees of success in predicting phase stability, but are still unreliable and far from universal application. It is indeed a complex problem to evaluate the small differences in free energy between the various possible stable configurations as a function of pressure and temperature. It is, however, of obvious interest to be able to predict phase behaviour for different conditions of pressure and temperature. In view of the inadequacy of a theoretical treatment the importance of the empirical crystal chemical approach is obvious. The latter necessitates a systematic experimental study of various simple systems in order to be able to generalize. Various empirical correlations based on atomic size and radius ratio, structure field maps,[20] heats of atomization, electronic configuration, close packing, electronegativity, coordination number, *etc.* have been obtained by systematic experimental studies. A review by Newnham[21] discusses these crystal chemical aspects of phase diagrams.

The present review will briefly describe work that has been going on in our laboratory and will highlight the remarkable similarity between the phase diagrams of certain groups of related compounds. A range of ionic compounds will be discussed. In addition, the determination of composition-temperature-pressure diagrams for binary alloys has shown interesting trends which depend on the phase relations of the end-members. Some of these trends will be reviewed.

2. Phase Relations for Groups of Related Inorganic Compounds

The similarity in the pressure-temperature phase diagrams of some compounds are remarkable. The most simple inorganic systems that have been studied are the alkali halides. These may be considered, to a first approximation, to consist of spherical cations and anions. These occur in the 6-coordinated NaCl-type structure that transforms to the 8-coordinated CsCl-type structure at higher pressures. This transition occurs at ~30 GPa for the sodium salts.[22] ~1.9 GPa for the potassium halides,[23,24] ~0.5 GPa for the rubidium halides[25] and at an estimated −0.5 GPa for the cesium compound (see Fig. 1). The empirical rule can be formulated as follows: For a given anion an increased cationic radius similates increased pressure, or similarly, the high pressure phases of compounds of the lighter cations simulate the structure of those of the heavier cations in the same group in the periodic table.

A change in the shape of the anion to the rod-shaped CN^- anion does not alter the high

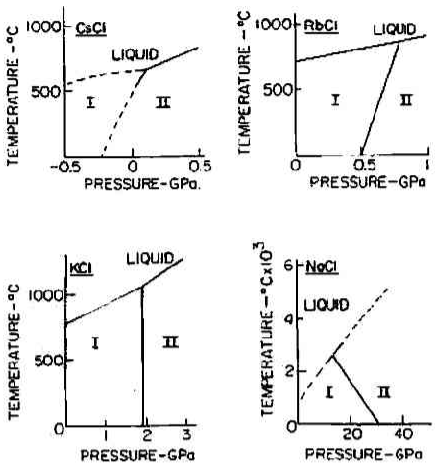

Fig. 1. High pressure phase diagrams of NaCl, KCl, RbCl and CsCl.

temperature phase behaviour observed in the alkali halides. The low pressure structure is still a 6-coordinated NaCl-type structure that transforms to an 8-coordinated CsCl-type structure with increased pressure.[26-31] The high temperature low pressure NaCl-type phase undergoes order-disorder transitions on cooling to a distorted NaCl-type arrangement. This mainly involves the thermal motion of the CN^- ions. The entropy change associated with these phase changes is mainly due to the change in configurational entropy caused by the change in the number of energetically equivalent and symmetry related positions that are available and over which the atoms can be distributed. This pattern holds for the alkali metal azides[32-34] and nitrites.[35-38] The phase diagram of KCN[39] is shown in Fig. 2. The NaCl/CsCl transition

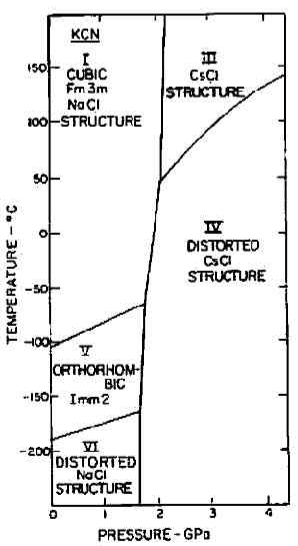

Fig. 2. High pressure phase diagram of KCN.

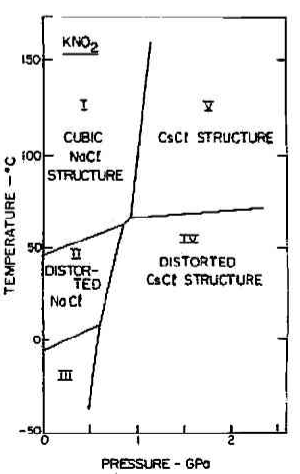

Fig. 3. High pressure phase diagram of KNO_2.

occurs near 2 GPa. For RbCN this occurs at ~0.6 GPa[39] while CsCN is in the CsCl-type phase at room pressure.[41] It, therefore, appears that the change in the anion, if compared to the alkali halides, has very little effect on the transition pressure of the NaCl-type phase to the CsCl-type phase.

On increasing pressure one would expect a trend to structural types with higher coordination numbers. A logical progression would involve coordination groups such as tetrahedral, octahedral, 8-coordinated, *etc.* By comparison with the above examples we would expect areas on the phase diagram where the coordination number remains essentially constant, but where order-disorder transitions intervene on increasing temperature.

The above arguments appear to hold even when the anion is changed to the non-linear V-shaped nitrite ion. The similarity between the phase diagrams of KNO_2 (Fig. 3)[42] and KCN (Fig. 2) is striking. The high temperature phases are similar, while the structural differences occur mainly at lower temperatures where the effect of the different chemical species anions is observed. The NaCl/CsCl-type transition appears at ~1GPa. Once again this transition is expected at negative pressure for the cesium salt. Furthermore, the structure of $CsNO_2$[43] is essentially the same as that of KCN IV and KNO_2 V.

Up to now we have considered relatively simple modifications to the spherical anion, but a most valuable comparison emerges for substantially more complex anions as is the case with the alkali metal perchlorates and tetrafluoroborates. This may be seen from Figs. 4 to 9 for $NaClO_4$,[44] KBF_4,[45] $RbBF_4$,[46] $CsBF_4$,[47] NH_4BF_4[48] and $TlBF_4$[49] respectively. The perchlorates have phase diagrams similar to the tetrafluoroborates, except that the former decompose at relatively low temperatures. The phase diagram of $CsClO_4$[47] is shown in Fig. 10.

Both $NaClO_4$[50] and $NaBF_4$[51] have an orthorhombic phase, space group Cmcm, with the

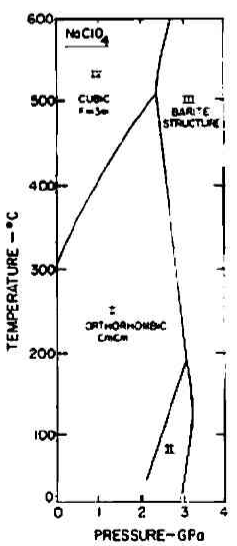

Fig. 4. High pressure phase diagram of $NaClO_4$.

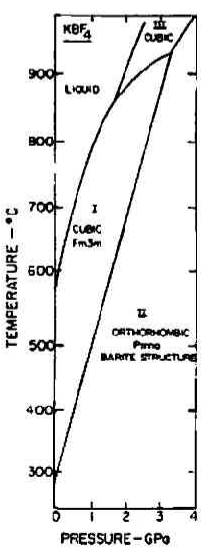

Fig. 5. High pressure phase diagram of KBF_4.

anhydrite structure at low pressure, which is not observed for the other alkali compounds. As in the case with the alkali halides one could imagine the phase to exist at negative pressures only. The cation coordination with respect to oxygen is 8, but 6 with respect to the centres of the tetrahedral anion. Pressure induces a transition to another orthorhombic phase, space group Pmna which has the barite structure.[41] In the case of $NaClO_4$ this proceeds *via* an interven ing phase that exists below ~180°C. In the barite phase the cation oxygen coordination is 12. In all the above-mentioned alkali metal compounds the ambient barite phase further transforms

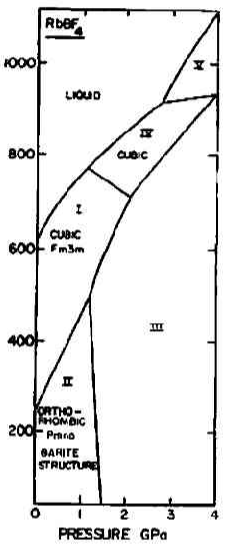

Fig. 6. High pressure phase diagram of $RbBF_4$.

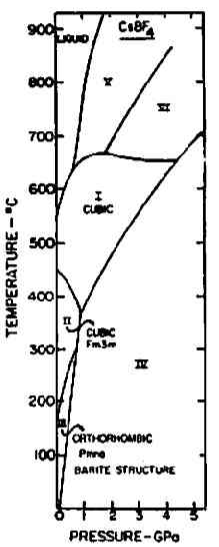

Fig. 7. High pressure phase diagram of $CsBF_4$.

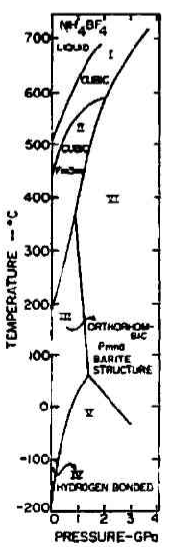

Fig. 8. High pressure phase diagram of NH_4BF_4.

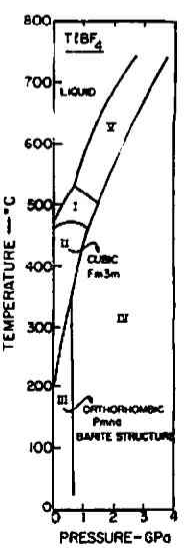

Fig. 9. High pressure phase diagram of $TlBF_4$.

to a NaCl related partly disordered cubic phase on increasing temperature, *i. e.* to $NaClO_4$IV, KBF_4I, $RbBF_4$I, $CsBF_4$II, $TlBF_4$II and NH_4BF_4II.

Free rotation of the anions probably does not occur in this phase. Additional phases with completely unknown structure do occur at still higher temperature for rubidium, cesium and thallium.

The KH_2PO_4(KDP)-type compounds also exhibit many interesting similarities. The similarities include isostructural phases, quasi-irreversible phase transitions and similar effects upon

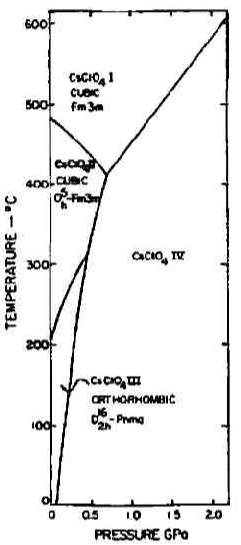

Fig. 10. High pressure phase diagram of $CsClO_4$.

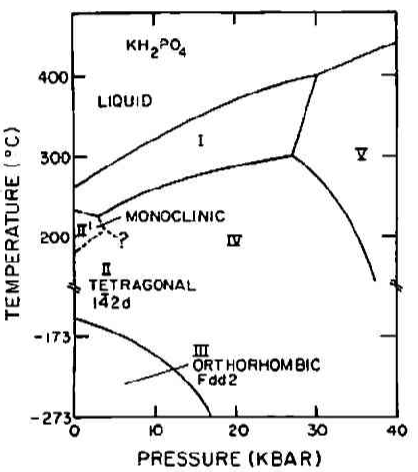

Fig. 11. High pressure phase diagram of KH_2PO_4.

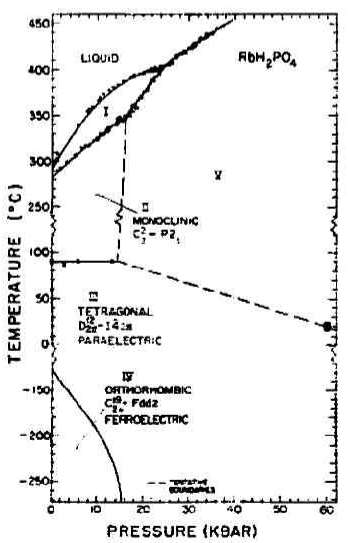

Fig. 12. High pressure phase diagram of RbH_2PO_4.

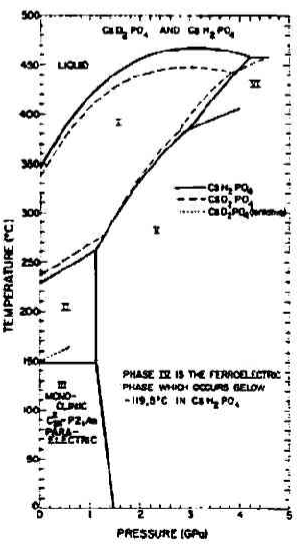

Fig. 15. High pressure phase diagrams of. CsD_2PO_4 and CsH_2PO_4

transition temperatures due to deuteration. To illustrate the similarities the phase diagrams of KH_2PO_4,[52] RbH_2PO_4,[53] CsH_2PO_4,[53] KD_2PO_4,[53] CsD_2PO_4,[54] $NH_4H_2PO_4$[55] and CsH_2AsO_4[56] are shown in Figs. 11-16. A clear understanding of any set of crystal chemical relationships depends on available structural information. Unfortunately the KDP-type compounds decompose at high temperatures and this has prevented structural data being collected.

One pattern that does emerge is that the low temperature orthorhombic ferroelectric phase (KDP III) transforms to a paraelectric tetragonal phase (KDP II) which transforms to a monoclinic high temperature phase (KDP II') by way of a complex quasi-irreversible phase transition. The high temperature phase KDP I eventually melts. RbH_2PO_4, CsH_2PO_4, $NH_4H_2PO_4$ and CsH_2AsO_4 show similar trends with the notable exception being the monoclinic paraelectric phase in CsH_2PO_4. High pressure phase behaviour for the group always includes a high volume change transition which is particularly sluggish at room temperature.

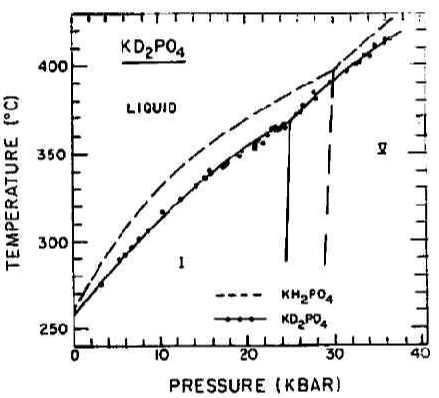

Fig. 14. High pressure phase diagram of KD_2PO_4.

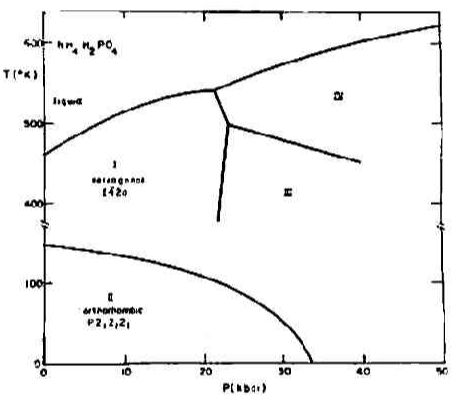

Fig. 15. High pressure phase diagram of $NH_4H_2PO_4$.

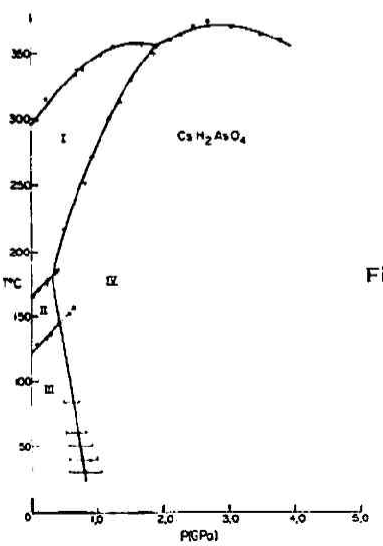

Fig. 16. High pressure phase diagram of CsH_2AsO_4.

The transition is located at about 1GPa for the group with $NH_4H_2PO_4$ and KH_2PO_4 showing a similar transition at higher pressures. Deuteration studies have revealed interesting behaviour patterns where melting points are depressed, while certain solid-solid transitions show the opposite effect. Deuteration does not however significantly change the basic phase diagram in any of the cases studied so far.

Numerous other examples exist of similarities in the phase diagrams of related compounds. Earlier examples are discussed in reviews by Klement *et al.*[1] and Pistorius.[2] The above correlations are for predominantly ionic compounds. Excessively polarizable ions and compounds of dominantly covalent character have shown fewer obvious similarities.

3. High Pressure Phase Relations for Binary Alloy Systems

The phase diagrams discussed so far have been for single component systems. The composition-temperature-pressure diagrams that have been reported have been for binary metal alloy systems, and examples include the Na-K,[57] Al-Ge,[58] Al-Si,[59] Cd-Mg,[60] Cd-Zn, Sn-Zn,[61] Cd-In,[62-63] In-Sb,[64] Bi-Sb,[65] Bi-Tl,[66] Bi-Cd,[67] Bi-Sn,[61] Bi-Pb,[68-69] Zn-Sb,[70-71] Cd-Sb,[72] Cd-Tl,[73] Cd-Sn,[74] Cd-As, Zn-As,[75] Pb-As,[76] Cd-Pb,[77] Pb-Sb[78] and others involving the III-V and II-VI elements.[79]

The studies of these systems consist of *in situ* DTA or resistivity studies and also of structural studies on quenched phases. The studies are aimed at determining the dependence of eutectic composition and temperature on pressure. The stability of phases present is an important factor and in some cases new compounds form, but in other cases intermetallic compounds disproportionate at high pressures *e. g.* CdSb,[70] CdAs and $ZnAs_2$.[75]

The pressure dependence of eutectic composition has always been a problem to observe experimentally. The direction of movement of the eutectic composition can be ascertained by

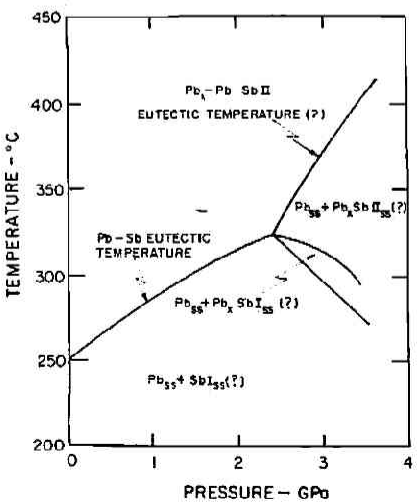

Fig. 17. High pressure phase diagram of the Pb-Sb eutectic.

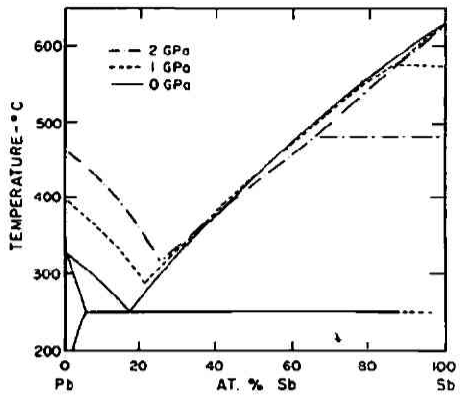

Fig. 18. High pressure phase diagram of the Pb-Sb system.

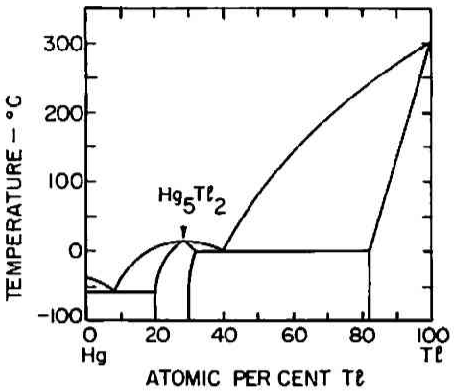

Fig. 19. Composition-temperature phase diagram of the Hg-Tl system.

studying alloy compositions straddling the initial eutectic composition with sensitive DTA techniques under pressure. If a composition is properly chosen the temperature difference between the eutectic and liquidus temperatures gradually reduces to zero with increasing pressure due to the eutectic composition approaching that of the experimental composition. When all the high pressure data are combined it is possible to construct a pressure-temperature-composition diagram as is shown in Fig. 18.[80] From this it is possible to determine the pressure dependence of the eutectic composition.

As a first example, let us consider the Pb-Sb system. The Pb-Sb system is a simple eutectic system with no intermetallic compounds.[80] The effect of pressure on the 17.7 at. % Sb, 251.2°C eutectic composition is shown in Fig. 17.[80] The eutectic temperature rises smoothly with pressure to 2.4 GPa and then rises sharply where a new high pressure phase becomes stable. If an alloy with the eutectic composition of 17.7 at. % Sb is subjectedto high pressure DTA experiments, it is observed that the initial single signal gradually dissolves into two signals on increasing pressure. This phenomenon is due to the fact that the eutectic composition is pressure dependent and that the experimental composition no longer corresponds to the eutectic composition at elevated pressure. The additional signal corresponds to the liquidus temperature at that pressure. All off-eutectic alloy compositions should, however, yield the same pressure dependence for the eutectic temperature, and this is confirmed experimentally.

Different eutectics display different pressure dependence. In contrast to the Pb-Sb system where the pressure dependence of the eutectic composition is ~4 at. %/GPa, the Hg-Hg_5Tl_2 and the Hg_5Tl_2-Tl eutectics, which are located at 8.5 at. % and 40 at. % Tl respectively in the Hg-Tl system (see Fig. 19),[81] display a minimal compositional pressure dependence.[82] It was found, however, that the mean pressure dependence of the eutectic temperatures are 41°C/GPa and 36.5°C/GPa respectively. If these results are combined with that of the melting curve of the intermetallic compound, Hg_5Tl_2,[83] which is located at 28.6 at. % Tl, and that of pure Hg[84] and Tl,[85-86] the pressure-temperature-composition phase diagram that is

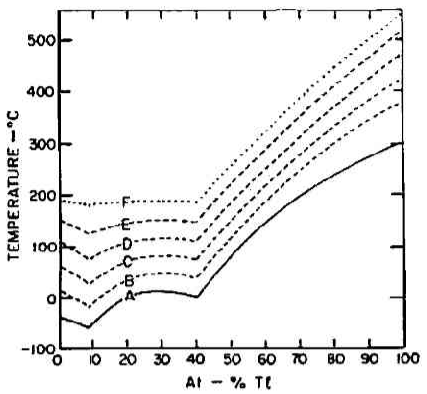

Fig. 20. High pressure composition-temperature phase diagram of the Hg-Tl system. (A=atmospheric pressure, B=1 GPa, C=2 GPa, D=3 GPa, E=4 GPa, and F=6 GPa)

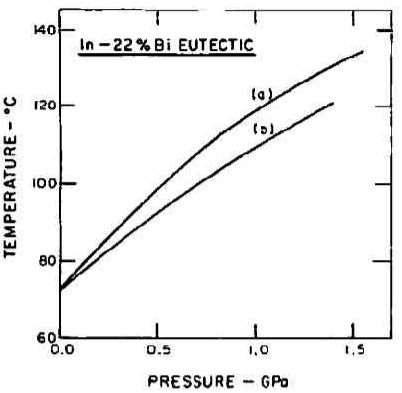

Fig. 21. High pressure phase diagram of the In-22 at. % Bi.

shown in Fig. 20[82] results. The effect of pressure is to flatten out the maximum in the liquidus curve corresponding to intermetallic compound Hg_5Tl_2. Extrapolation of 4 GPa data suggests that the maximum would level out at ~6 GPa. This could imply that at higher pressures a continuous solid solution could exist between fcc Hg_5Tl_2 and an expected fcc high pressure phase of Hg.[84] Furthermore, Tl transforms to a fcc high pressure phase above ~9 GPa. It is therefore possible that a wide range of solid solubility could exist at high pressures over the entire composition range. However, at atmosheric pressure solid Hg_5Tl_2 is ~3% less dense than the corresponding mixture of solid Hg and liquid Tl at atmospheric pressure and it may therefore be destabilized at pressures where the melting temperature of Hg is below that of Hg_3Tl_2.

An example of a more complex system is the In-Bi system which has 3 intermetallic compounds, *i. e.* In_2Bi, In_5Bi_3 and InBi with the In-In_2Bi and InBi-Bi eutectics located at 22 and 52.7 at. % Bi respectively.[81]

On increasing pressure both eutectics move to higher Bi content.[87] Fig. 21 illustrates the increasing temperature difference between the eutectic and liquidus temperatures as the 22 at. % eutectic composition changes with pressure from the initial starting composition of 22 at. %. Figure 22 confirms that this change is towards a higher Bi content as the initial temperature difference of the off-eutectic composition of the 33 at. % alloy decreases with pressure until the eutectic and liquidus temperatures merge at 133°C, 1.83 GPa where the 33 at. % alloy becomes the eutectic composition. A new high pressure phase is stable above these pressures and causes the eutectic temperature to rise more steeply with pressure (Fig. 22 curve (c)). This phase is also observed for alloys with 50 at. % (InBi) (Fig. 23), 52.7 at. % (Fig. 24) and 57 at. % Bi content[87] (Fig. 25).

The composition of the InBi-Bi eutectic is also pressure dependent but the eutectic temperature is relatively insensitive to pressure (Figs. 24-26 curves (b)). The initial single eutectic

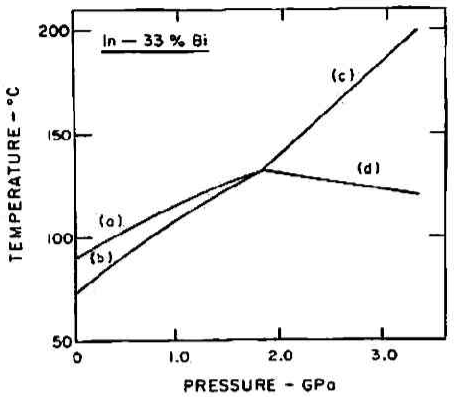

Fig. 22. High pressure phase diagram of In-33 at. % Bi.

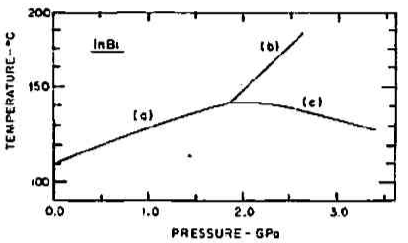

Fig. 23. High pressure phase diagram of InBi.

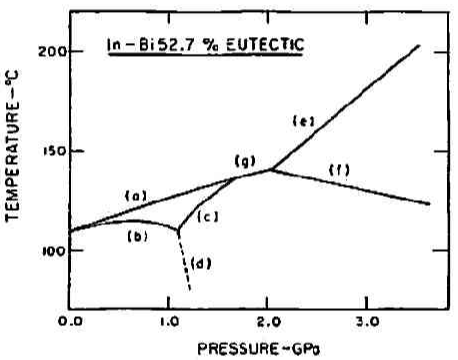

Fig. 24. High pressure phase diagram of the In-52.7 at. % Bi eutectic.

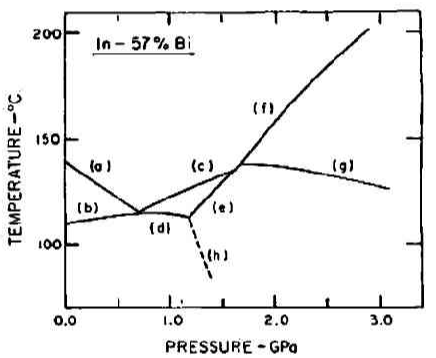

Fig. 25. High pressure phase diagram of In-57 at. % Bi.

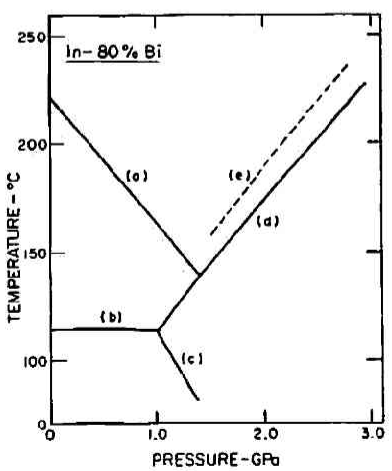

Fig. 26. High pressure phase diagram of In-80 at. % Bi.

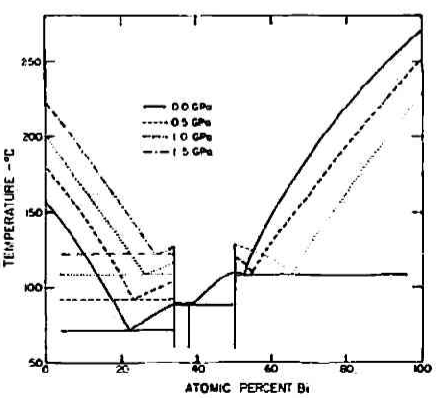

Fig. 27. High pressure composition-temperature phase diagram of the In-Bi system.

signal at atmospheric pressure splits into eutectic and liqudus curves with pressure (Fig. 24 curves (a) and (b)) but an intervening high pressure phase boundary (Fig. 24 curve (d)) causes the eutectic temperature to rise and to meet the liquidus curve again at 1.6 GPa, 135°C. The 52.7 at. % Bi alloy therefore again becomes the eutectic composition at 1.6 GPa. The high pressure phase, the so-called X-phase, displays super-conducting properties[88,89] and is probably isomorphous with similar phases that appear in the Bi-Sn and Bi-Pb systems.[88,89-91] Indications of this phase were observed for alloys with composition 52.7, 57 and 80 at. % Bi and it probably exists over the composition range between InBi and Bi.[87] From Fig. 25 it is clear that the initial 52.7 at. % Bi eutectic moves towards higher Bi content with pressure as the 57 at. % alloy has the eutectic composition at ~0.7 GPa where the liquidus (a) and eutectic curves (b) converge. A further increase in pressure causes the eutectic and liquidus curves to move apart again (Fig. 25 curve (c) and curve (d)), but due to the influence of the phase boundary of the X-phase (curve (h)) the eutectic temperature rises again (curve (e)) and meets the liquidus curve at 1.6 GPa, 136°C to form a eutectic at this point. Curves (f) and (g) delineate a high pressure phase which is probably iso-structural with the high pressure phase of InBi (Fig. 23). The 80 at. % Bi alloy becomes the eutectic composition at ~1.4 GPa. A comparison of the various figures with the melting curves of InBi and Bi seems to indicate that alloys with higher Bi concentrations display phase behaviour oriented towards that of Bi, while alloys with lower Bi concentration show more InBi character. Furthermore, the similarity between the curves (b), (d) and (b) of Figs. 24, 25 and 26 respectively is observed, as these represent the same phase boundary, similarly for curves 24 (c), (g) and (e), 25(e), (f) and 26 (d).

The theoretical calculation of the pressure-temperature-composition phase diagrams of non-unary metal alloy systems from fundamental theory may be expected to be even more involved than that of the single component systems. However, various degrees of success have been attained from semi-empirical and pseudo-potential calculations[92] of high pressure phase equilibria and by considering the free energies of the various phases as a function of temperature and composition.[93-95] At high pressures the PV contribution terms should be incorporated into the expressions for the atmospheric pressure free energy. In addition, lattice stability, pressure, size and also electronic, vibrational and magnetic contributions should be taken into account. A large number of binary alloy systems have been considered and at present it appears that the factors limiting the accuracy are the numerical values for the lattice stability and interaction parameters, together with the uncertainty of the excess free energy when employing regular solution theory.[96] Much of the needed data is obtained from experimental techniques such as splat cooling, vapour deposition techniques, studies of metastable phases and from high pressure phase diagrams.

4. Conclusions

The review has discussed phase behaviour of groups of related inorganic compounds and of

metal alloy systems. The similarities between the high pressure phase diagrams of families of compounds are pointed out and discussed for the alkali halides, cyanides, nitrites, perchlorates, tetrafluoroborates and also for the *di*-hydrogen phosphate and arsenate groups and their deuterated analogues.

The binary metal alloy systems that are considered are the Pb-Sb, Hg-Tl and In-Bi systems. The effect of pressure on the eutectic compositions and temperatures are illustrated and the behavioural trends discused.

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